

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR
WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS

PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of Irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34, Example 1).

5. Prior to January 20, 1995, we conceived of various embodiments of the invention, that is irradiation of UHMWPE combined with melting, as described in item C of Premnath Venugopalan's note (see Exhibit 1). At the time, we believed that a prosthesis formed out of UHMWPE bar stock that had been heated above the melting point and irradiated (in air or an inert environment) in that molten state (see item c), or had been irradiated and then heated above the melting point, would form cross-links (see item b). The increased mobility of the molecules in the molten state allows the free radicals to combine with each other and form cross-links, as opposed to remaining in a trapped state.

6. Prior to January 20, 1995, we continued conducting melt-irradiation (MIR) experiments at Mr. Kenneth Wright's laboratory (the High Voltage Research Laboratory (HVRL), located in building N-10 of M.I.T. at 155 Massachusetts Avenue, Cambridge, MA 02139. Mr. Kenneth Wright was responsible for the day-to-day operation and

management of the radiation applications activities of the HVRL, including scheduling, operation, maintenance of equipment and research with the Van de Graaff accelerators). Six UHMWPE samples were irradiated at 1.0, 2.5, 5, 10, 20 and 50 Mrads by Mr. Ken Wright. The samples were heated to melt and irradiated while in a molten state. Subsequently, MIR experiments using solid bars in sealed containers (sealed glass vials) were done at Mr. Wright's laboratory. Copies of Mr. Wright's laboratory logbook page numbers 122-123 and 126-127 containing the record of MIR work done are attached as Exhibit 2. A copy of the corresponding page 10 of lab book no. 2 is attached as Exhibit 3.

7. Also, prior to January 20, 1995, we conducted a thermal analysis of the irradiated UHMWPE specimens, as described in paragraph 9, by use of DSC. This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity.

Six polymer samples, as described in paragraph 9, also were irradiated in sealed pans for crystallinity analysis. The samples were heated to melt and irradiated while in a molten state. A copy of Premnath Venugopalan's laboratory note book page numbers 8-9 is attached as Exhibit 3 (see Expt 1 and Expt 2). Thus, prior to January 20, 1995, we have practiced the process of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state. The DSC testing on the polyethylene samples that were irradiated in a molten state was conducted. Crystallinity levels had dropped to 37.77% (printed as 37.8%) for the sample given a 20 Mrad radiation dose. Copies of the corresponding DSC data sheets are attached as Exhibit 4 (marked as 'data-6'). Crystallinity data from unirradiated GUR415 bar stock was used as control. Irradiation dose (20 Mrad), temperature (125.51, printed as 125.5) and crystallinity data (37.77%, printed as 37.8%) from this work are presented in a patent application that became the '400 patent (see, for example, Table 1 on column 9 of the '400 patent), in the '313 application (see, for example, Table 1, page 27), and the '638 application (see, for example, Table 1, page 35).

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ESR results indicated no detectable free radicals in melt-irradiated polyethylene, whereas the control polyethylene that was irradiated at room temperature without concurrent or subsequent melting showed the presence of free radicals. The absence of free radicals in the melt-irradiated polyethylene indicates that any further oxidative degradation would be avoided, and thus the material was suitable for use in medical prostheses. See Exhibit 5 for ESR spectra from an experiment conducted prior to January 20, 1995. The ESR spectra show samples irradiated at room temperature contain free radicals; whereas, the samples irradiated at 175°C do not have any detectable free radicals.

Swell Ratios indicated that the melt-irradiated polyethylene was highly crosslinked and did not allow dissolution of polymeric chains, while unirradiated polyethylene dissolved completely, which signifies lack of cross-linking in the unirradiated polyethylene. See Exhibit 6 for swell test results of an experiment conducted prior to January 20, 1995. Swell test data shows control specimens dissolve completely within 24 hours in DecalinTM at 150°C.

9. The above testing confirmed that we had invented, among other things, (1) methods of making an improved prostheses by combining melting and irradiating to cross-link UHMWPE, and (2) improved prostheses that were the result of these processes. These prostheses are wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

Cross-linking by irradiation at room temperature and subsequent melting

10. Prior to January 20, 1995, we also developed another embodiment to preserve the highly disordered entangled state of the UHMWPE in order to solve the wear problem (see item b of Exhibit 1). The embodiment involved cross-linking the polyethylene in at room temperature ('cold irradiation') by irradiation and subsequent melting. The process is referred to as Cold-irradiation and Subsequent Melting or "CISM " and is disclosed in U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 39, Example 8), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 47-48 , Example 8).

11. According to this embodiment, UHMWPE is irradiated at room temperature to cross-link and subsequently the irradiated UHMWPE is heated above the melting point of about 135°C and then cooled. This process subsequently referred to as cold irradiation and subsequent melting or "CISM", meaning irradiation of UHMWPE at about room temperature and then heating the irradiated UHMWPE above the melting point and resolidifying.

12. Prior to January 20, 1995, we had a number of UHMWPE specimens irradiated at room temperature at Mr. Kenneth Wright's laboratory. A copy of Mr. Wright's laboratory logbook pages number 120-121 containing a log of irradiation work done prior to January 20, 1995 is attached as Exhibit 2. The experiment (Marked as Irradiation Experiment 1) and the process including radiation doses used are recorded in lab note book no. 2, page no. 8. A copy of the laboratory note book page number 8, which is attached as Exhibit 3.

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measured. The cycles include of heating the specimen to a temperature above its melting point, cooling down to room temperature, and heating again to a temperature above its melting point. The first cycle of this DSC method, involved heating and cooling, was applied to the room temperature irradiated UHMWPE test specimens, as described in paragraph 10 above. Therefore, we practiced the "CISM" process prior to January 20, 1995. The DSC test results indicated that the crystallinity levels decreased from approximately 54.71% present in the starting material to as low as 41.69% when irradiated at 20 Mrad. A copy of that data sheet is attached as Exhibit 4 (see sheet marked as 'data-4') and the corresponding DSC data sheet is attached as Exhibit 4. This reduced crystallinity confirmed our view that the "CISM" method also would improve the structure and wear resistance of the UHMWPE by decreasing the content of chain-folded crystalline lamellae, which otherwise would lead to fibril formation.

The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that wore the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

April 14, 2004
Date

Date

Date

Date

Date

Date

Edward W. Merrill
Edward W. Merrill

William H. Harris

Premnath Venugopalan

Murali Jasty

Charles R. Bragdon

Daniel O. O'Connor

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We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

Date

3-5-04 (3 May 04)

Premnath Venugopalan

Date

Murali Jasty

Date

Charles R. Bragdon

Date

Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR
WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS

PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34, Example 1).

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Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

Date

4/22/04

Murali Jasty
Murali Jasty

Date

4/21/04

Charles R. Bragdon
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Date

Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s): Edward W. MERRILL *et al.*

Confirmation No.: 7398

Serial No.: 10/197,209

Examiner: Susan W. Berman

Filing Date: July 18, 2002

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The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

Date

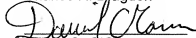
Murali Jasty

Date

5/19/04

Date

Charles R. Bragdon



Daniel O. O'Connor

EXHIBIT - 1

BULK CROSS-LINKING FOR IMPROVED UPE PROPERTIES

↳ starting

BASIC MOTIVATION :-

It is clear that as mol. wt. of PE increases, its abrasion resistance increases. Further as hypothesized by Prof. Merrill, the increase in entanglements should reduce wear. ~~Both ways~~ ^{there seems to be an effort at} increasing the resistance of PE chains to ~~being~~ ^{being} pulled out of the bulk.

Hence, the following treatments ~~are~~ are being considered as ways to increase the resistance faced by PE chains against being pulled out:

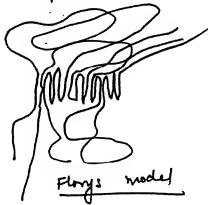
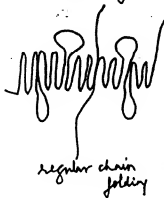
(a) Heat and rapid cooling: Heat the polymer to a completely disordered ~~state~~, highly entangled state and then suddenly cool it ~~down~~ in order to trap it in that state.

This may be possible with 10 μ thick films dipped into liq. N₂ but is not possible for larger specimens (Researchers have used several 100 to 100,000 °C/min). Further there are problems of differential crystallization at different positions and problems of sapon concentrations.

(b) Crosslink as solid, melt, recrystallize: Irradiating the polymer as a solid will mean ~~less~~ ^{concentration} crosslinking at the crystalline zones but higher crosslinking in the amorphous zones (more mobile chains can ~~more~~ jump more to connect at different places). Melting & recrystallizing these will probably again lead to the original crystal structure ~~but~~ (though with reduced crystallinity) ~~the~~ and selective segregation of crosslinks into the amorphous regions. This is expected to be more wear resistant since molecules in the tie regions may be interconnected & crosslinked. Promises to be useful if (a) inter crystalline region slip is

important during wear (2) if loss in hardness is not crucial.

(c) Crosslink as melt, recrystallize: More reduction in crystallinity expected with uniform crosslinking (much more than in x-linking of the solid). More likely that chain-folding in the Flory sense ^{will occur} where ~~chains do~~ ~~not fold~~. Instead of one chain folding repeatedly, ~~because~~ many chains will fold in a given region. Here ~~the~~ the amorphous region will have more interconnected regions, x-link points & longer loops.



(d) Crosslink the solid:

~~the~~ Hardness of original UPE is retained and hopefully there will be ~~more~~ selective crosslinking in the amorphous regions.

Questions/Concerns:

① Degradation vs. Crosslinking
↓
Mol wt ↓
Xcristallinity ↑
Wear ↑
Free radicals
(long-term existence)

↓
Extent ?

② Crosslinking vs. Crystallinity
↓
decreases as
xlinking ↑ (if recrystallized)

③ Crosslinking vs. Crystal structure

Ideas:

① Crosslinking by irradiation of
Hylamer after it has been processed
and no recrystallization. || ⇒ highest crystallinity
+ Crosslinking.

② Study crosslinking in HDPE instead to see
extent of unlinking, degradation etc.

IRRADIATED SPECIMENS
FROM ZIMMEL

$$1 \text{ Mrad} = 10^4 \frac{\text{erg}}{\text{g}} = 10^8 \frac{\text{erg}}{\text{g}}$$

$$10^{-7} \frac{\text{J}}{\text{g}} = \text{erg}$$

$$10^{-2} \text{ erg} = \text{rad}$$

↓

$$\frac{\text{J}}{\text{kg}}$$

$$100 \text{ rad} =$$

$$1 \text{ Gray} = 1 \frac{\text{J}}{\text{kg}} = \frac{10^{17} \text{ erg}}{10^3 \text{ g}}$$

Data 2

DSC RESULTS: Effect of freezer-milling
and Effect of crosslinking by irradiation

Sample	T _{onset} (°C)	T _c (°C)	T _{peak} (°C)	% Cryst 1	% Cryst 2	Difference in Crystallinity	Avg. Lamellar Thickness 1	Avg. Lamellar Thickness 2
(Q1) GUR 415 - CONTROL	135.83	122.80	127.52	62.91	46.42	16.49	2.81×10^{-6}	1.51×10^{-6}
(M11) GUR 415 - FREEZER- MILLED - 10 min.	121.84	154.11	104.47	0.28 So low a % crystallinity? Again low order after heating?	0.57	-0.30	1.15×10^{-6}	0.653×10^{-6}
BAR - CONTROL	127.39	121.71	126.57	52.92 Nearby crystallites	41.37	6.55	1.52×10^{-6}	1.44×10^{-6}
BAR - 10 Mrad	130.53	127.95	119.05	54.02	45.29	8.73	1.84×10^{-6}	1.02×10^{-6}
BAR - 20 Mrad	111.05	120.48	110.78	54.95	41.69	13.26	2.05×10^{-6}	1.05×10^{-6}

EXHIBIT - 2

1.45

COOP COMPUTATION BOOK

NAME	NUMBER
KEN WRIGHT	1

Course F-12-50

Used from _____ to _____

HARVARD COOPERATIVE SOCIETY
1400 MASS. AVE., CAMBRIDGE, MASS. 02138TECH. COOP
84 MASS. AVE. CAMBRIDGE, MASS. 02139

Mumill	10	2.5	41	15	61	75	1.3	1.25×10^6
Beitrand	1-2	2.5	39	-	-	90	-	1.25×10^6

PEO collagen Peraz	1-9	2.5	62	24	1.1	430	1.3	2×10^6
Colagenon millipore filter	1-6	-	-	-	-	-	-	-

150 Liters Liquid N₂

PRIMA	Earl Williams	1	2.5	20	8.1	1.1	40	3.2	2.5×10^6
1/4" dia discs	1/2" thick	2	-	26	10.2	-	-	-	3×10^5
		3-5	-	26	-	-	-	-	-
		6-8	-	-	-	-	-	-	-
		9-10	-	17	6.4	-	58	-	2.5×10^5
	1/8" thick	11	2.0	33	10.2	-	90	-	3×10^6
		12-15	-	39	11.9	-	90	-	5×10^6

1-3 Garter	Schmitt	1-18	2.5	39	15	1.1	400	1.3	1.25×10^6
4-13	Schmitt	1-13	-	-	-	-	-	-	2.5×10^6
concentration		2-8	-	-	-	-	200	-	5.5×10^6

Thin Alms Polyurethane	1-3	-	30	12	-	100	1.3	10^6
Mumson Muskth 4-6	-	-	-	-	-	-	-	7.25×10^6
3-2108, Rm 35-352	-	-	-	-	-	-	-	-

Small (6.5 cm) Premnath Venkayappa	1-6	2.5	29	15	1.1	75	1.3	1.25×10^6
dia) cups	2-8	-	-	-	-	-	-	-
	2-8	-	-	-	-	-	-	11
	4-5	-	52	20	-	-	-	111
	5-6	-	63	29	-	-	-	2×10^6 HH
	6	-	-	-	-	-	-	HH
	6	-	-	-	-	-	-	HH
	6	-	-	-	-	-	-	HH

Shuck	Tubo MB Med Centre	1-4	2.5	33	13.6	-	430	1.3	10^6
		-	-	-	-	-	-	-	11
		-	-	-	-	-	-	-	11
		-	5-8	-	-	-	-	-	11
		-	-	-	-	-	-	-	11
		9-12	-	68	27	-	-	-	2.5×10^6

Varying strip	Schmitt	1-6	-	38	15	-	125	-	1.25×10^6
base for		1-6	-	-	-	-	-	-	-
		1-3	-	-	-	-	-	-	11

16 overlay (sufficient liquid overlay)

525x10⁶

6 hrs cover overlay

2 P6 over central area

No Ph.

2 overlays

525x10⁶ *turned over

525x10⁶

525x10⁶

525x10⁶

510

525x10⁶

525x10⁶

525x10⁶

525x10⁶

525x10⁶

525x10⁶

2 overlays

525x10⁶

525x10⁶

525x10⁶

1. 1st overlay may be slightly less than 5

525x10⁶

Polyethylene + Gueiro Schmitt 1-2 2.6 50 20 1.1 6.5 10^6

Acetone, thinner

PEO in Petri dishes Stephanie 1-10 2.6 30 12 1.1 250 1.3 10^6

and Cinnabar

Stephani Lopina 1-15 - 60 24 - 340 - 2×10^6

3-7115 1-20 - - - 440 -

354-7489

Book - wetter + Chat Cooke 1 2.6 60 24 1.1 160 1.3 2×10^6

2 - - - - -

3,4 - - - - -

PEO in 6" (1-15) Ken Breckner 2.1 176 6.8 1.0 100 2.2 2×10^6

(Finetel) B. U.

Dept of Astronomy 7-12 - 176 6.1 -

17-32, 725 Comm. Ave 15-72 180

Cyber + other shops 02215 33-42 180

353-2625

8.5

PTFE + Polyethylene 1-3 4 37 18 1.1 140 1.7 1.25×10^6

PEO#

PEO in Petri dishes sac 1-20 4 30 12 1.1 440 1.3 10^6

above

and Cinn

1-15 - 60 24 - 360 - 2×10^6

Polyethylene Premnath Varugapala 1-4 2.8 70 30. - 85 - 2.5×10^6

over ketoplate

1-3 - - - - -

1-2 - - - - -

1 - - - - -

- - - - -

- - - - -

See above Stephani Lopina 1-15 2.6 30 12 1.1 355 6.3 10^6

Polyethylene Premnath Varugapala 1-8 2.6 37.5 15 - 135 1.3 1.25×10^6

1-4 ketoplate

1-3, 5 5 2

1-2, 3, 6 2.8 52 24 - 105

1, 5 - - - - -

1 - - - - -

- - - - -

PEU soln ~~PEO~~ PTFE Schmitt 1-20 2.6 37.5 15 - 165 1.3 1.25×10^6

Polyethylene Premnath

* small beads 1-6

1-4, 6 5 2

1-9, 1-10 5 2

1-20 5 2

1-3, 1-4 5 2

1-3, 1-4 2.75 47 20 -

1-4, 1-5 2.75 47 20 -

1, 1 2.75 47 20 -

- - - - -

- - - - -

- - - - -

- - - - -

- - - - -

- - - - -

180L N:

Zurlo

Z2x10⁶

Turned over for Z2nd run

1 discharged

Petrin with 5 glass cubes

Z2x10⁶Z10⁷Z2x10⁷Z5x10⁷Z5x10⁷Z2x10⁶

Z20 1st run hot plate jammed before irradiation - activated and passed through

Z9.8x10⁶Z10.8x10⁶Z13.2x10⁶Z17.2x10⁶Z2.5x10⁶Z3.75x10⁶Z5x10⁶Z10⁷Z2x10⁶Z3.5x10⁷

EXHIBIT - 3

Student's Name

Date

8

Subject

Instructor's Name

Irradiation
Studies.

→ e^- beam
at HVRL, MIT.

Kenneth A. Wright.

Student's Name

Date

8

Subject

Instructor's Name

EXPT (1) → Irradiation of solid polymer (PE) from bar stock

~~Irrad/RT/low/RT/High/RT/low~~Set 1Set 2

↓
12 samples
of thickness of a
few microns kept
between two slides

↓
6 samples in
DSC pans

RT

1.0 MRad	(each)
2.5 MRad	
5.0 MRad	
10.0 MRad	
20 MRad	
50 MRad	

RT

1.0	MRad
2.5	"
5.0	"
10.0	"
20.0	"
50.0	"

↓
This was for
studies under
polarizing
microscope
at MGH

↓
DSC Runs done
& results in
the file (# 3)

↓
Result → all

... showed ...
spherulites
on melting & cooling
under microscope

Subject

Instructor's Name

EXPT. (2) Irradiation of barstock while a melt.

Irrad. / TSC / Air / No follow AT / PANG

F.M.H.T.

6 Samples → 1.0, 2.5, 5, 10, 20, 50 MRads.

at temp. $> 150^{\circ}\text{C}$

Range (155 to 180°C approx.)

Heating → Sample heated ~~approx once~~ intermittently.

Heated → 1.0 MRad → Heated → 2.5 MRad

10 MRad ← Heated ← 5.0 MRad ← Heated

↓
Heated → 20 MRad → Heated → 35 MRad↓
Heated
50 MRad

Samples placed on a heated Al plate (Link)

Analysis → In file #3:DSC Error:Dose

1

2.5

5

10

20

50

mg

9.732

11.433

9.540

9.061

10.133

11.638

There was some confusion because the heating caused the marks on the pans.

Weights were correlated by measuring ~~separately~~ ^{separately} ~~apart~~ ^{apart} from another.

the weights were well distributed and each far apart from another.

Student's Name

Date

Subject

Instructor's Name

EXPT. 3: Irrad. / 75°C / N_2 atm / NO follow-up HT / VIALS

→ FUHT

Samples :- Barstock (from surface) \rightarrow constant radius. ~~of~~
Samples 4ms - 2.5 to 3cm radii

4 samples \rightarrow $2.5, 10, 20, 50$ MRad

Method :- Thin strips in vials.

Vial filled with N_2 as in heat treatments.

Heater used this was small enough to fit
under generator outlet
(heater provided by Prof. Merrill)
cooling in air (room temp.)

Sample left in ^{vial with} N_2 atmosphere at R.T. after irradiation.
for >5 days

Analysis

Student's Name

10

Subject

Instructor's Name

EXPT 4: Irrad / ITS C / Air / NO FUHT / VIAL

Samples: Bar Stock (b/w 2.5 to 3 in radial distance)

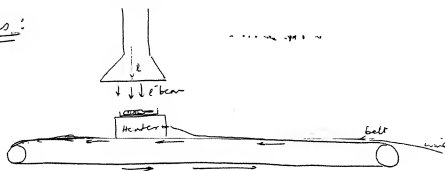
4 Samples \rightarrow 2.5, ^(9.8)~~2.5~~, ^(9.8)~~2.5~~, 50 M Rad.

Method: (As in previous page)

Analysis

: E. 79x3

Apparatus:



Student's Name

Date

10

Subject

Instructor's Name

EXPT 5: Inrad/RT/N₂/NO-FURT/VIALSample → Same as last page.Method → Same as last page.~~EXPT 5~~

	One	MRad
①	0.5	"
②	0.8	"
③	10.8	"
④	50	"
⑤		
⑥		

EXHIBIT - 4

E-IRRADIATION OF
THE MELT.

E-IRRADIATION OF THE MELT

Procedural Details:

The following experiment was performed at HVRL, MIT. The points to be noted ~~are~~ as follows:

- (1) Since the hot plate would not fit under the Van de Graaff generator, the specimens ^{in DSC pans} were placed in between two petridishes and laid on a metal plate acting as a heat sink while heating ~~to~~ (supplies heat when placed on the belt).
- (2) The heating was done at intervals ~~between~~ ---

- Start
- After 1.0 Mrad
- " 2.5 Mrad
- " 5.0 Mrad
- " 10.0 Mrad
- " 20.0 Mrad
- " 30.0 Mrad
- After 40.0 Mrad

- (3) It can be ~~assumed~~ assumed that approximately the temperature of the specimens was between 150-200°C

NOTE:

- ① Absence of bimodal distribution during crystallization

→ because no crystals during irradiation,

One phase:

(Swiss & X-ray is diffn. in crystalline regions)

- ② Since lamellar size and crystallinity $\propto T_m$ decreases,
 (crystal size)
 significant crosslinking occurring in proportion to scission.

If too much scission compared to crosslinking

→ mol wt would decrease

→ crystallinity & crystal size will increase

(e.g.) HDPE → 60%

Data 6

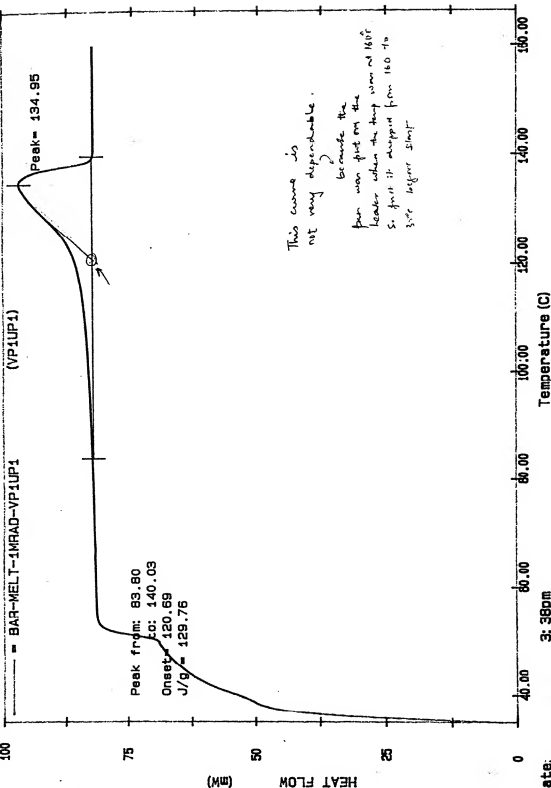
Label	Time	Height ft. above the shore	Angle of sight	Tc	Track	Time	% light 2 handline distance covered	Comp. diff.	Remark.
1	6:00	1.10	5	125.25	170.25	170.00	8.00	2.35	
2	6:05	1.11	5	125.25	118.51	119.23	11.05	2.25	
5	6:08	1.11	5	125.11	96.21	96.00	11.22	1.90	
10	6:09	1.00	4	118.35	83.21	83.23	10.11	2.50	
20	6:10	566.0	5	90.50	51.11	117.35	9.50	1.1	No second valley during x sailing
50	6:00	634.0	5	105.50	81.10	100.51	0.47	1.1	No second valley during x sailing

Quaking dew. dew. dew. dew. dew. dew.

- Note:
- ① Crystallinity is down below 40% for the first time.
 - ② Sudden drop in T_m (as in irrad. of solid PO) after 200 rad. (8th T_m & T_m2)
 - ③ Temp. consistent but decreasing an rad. dis increased (8th T_m & T_m2)
 - ④ Original R_{cr} $50\% \rightarrow 55\%$
Irrad. well & stability $\rightarrow 30-45\%$

will convert to
seconds

DATA



Date: 3:38pm
 Scanning rate: 10.0 C/min
 Sample Wt: 9.732 mg Path: C \ PE
 File #: VP1UP1 PRENT

PERKIN-ELMER DSC7

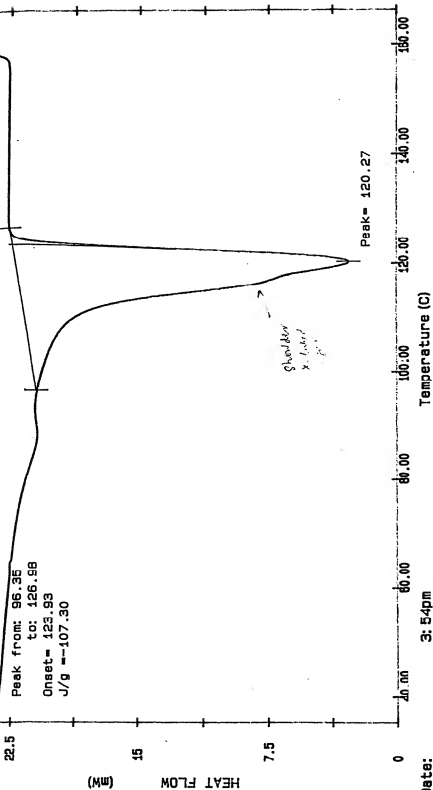
[illegible]

INNOVATIONS FOR ANGLES

Points MI	CONST OFF
132.82	-1.78
132.81	-28.30
132.80	-28.30
132.79	-28.30
132.78	-28.30
132.77	-28.30
132.76	-28.30
132.75	-28.30
132.74	-28.30
132.73	-28.30
132.72	-28.30
132.71	-28.30
132.70	-28.30
132.69	-28.30
132.68	-28.30
132.67	-28.30
132.66	-28.30
132.65	-28.30
132.64	-28.30
132.63	-28.30
132.62	-28.30
132.61	-28.30
132.60	-28.30
132.59	-28.30
132.58	-28.30
132.57	-28.30
132.56	-28.30
132.55	-28.30
132.54	-28.30
132.53	-28.30
132.52	-28.30
132.51	-28.30
132.50	-28.30
132.49	-28.30
132.48	-28.30
132.47	-28.30
132.46	-28.30
132.45	-28.30
132.44	-28.30
132.43	-28.30
132.42	-28.30
132.41	-28.30
132.40	-28.30
132.39	-28.30
132.38	-28.30
132.37	-28.30
132.36	-28.30
132.35	-28.30
132.34	-28.30
132.33	-28.30
132.32	-28.30
132.31	-28.30
132.30	-28.30
132.29	-28.30
132.28	-28.30
132.27	-28.30
132.26	-28.30
132.25	-28.30
132.24	-28.30
132.23	-28.30
132.22	-28.30
132.21	-28.30
132.20	-28.30
132.19	-28.30
132.18	-28.30
132.17	-28.30
132.16	-28.30
132.15	-28.30
132.14	-28.30
132.13	-28.30
132.12	-28.30
132.11	-28.30
132.10	-28.30
132.09	-28.30
132.08	-28.30
132.07	-28.30
132.06	-28.30
132.05	-28.30
132.04	-28.30
132.03	-28.30
132.02	-28.30
132.01	-28.30
132.00	-28.30

BAR-MELT-1MRAD-VP1DN1

(VP1DN1)

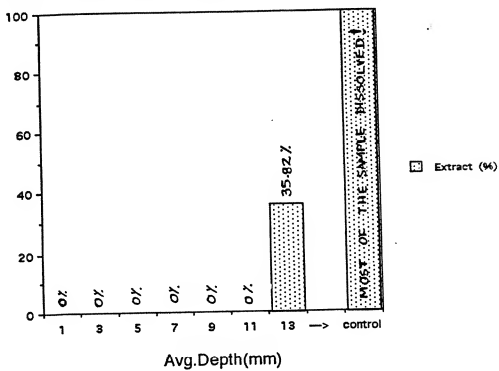


Date: 3:54pm
Scanning Rate: -10.0 C/min
Sample Wt: 9.732 mg Path: C:\PE\1
File 1: VP1DN1 PRENT

PERKIN-ELMER DSC7

EXHIBIT - 5

Extract percent in Decalin at 150 C (Samples from axis of irradiated cup 3)



Results from swelling test in Decalin at 150 C (Samples from axis of irradiated cup 3)

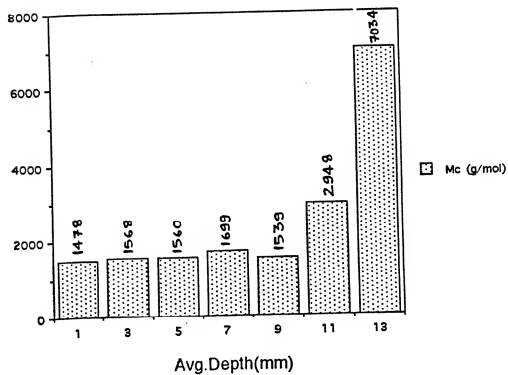
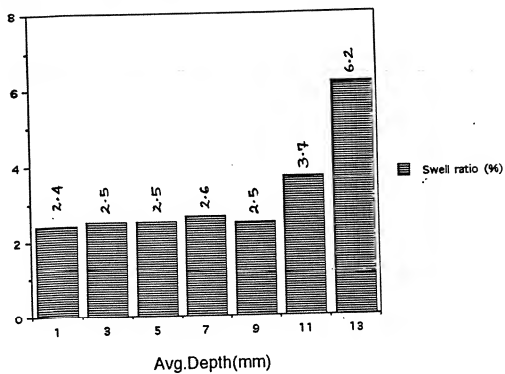


EXHIBIT - 6

198 Date

Tony Medeiros for Remotes

UNIVERSAL CHARTS

Sample: Bar Sample, Simulated as solid at RT

4% Phosphorus in

1 mV

Microphone Power

2.10⁴

Modulation Amplitude

4 MHz

Modulation Frequency

100

Modulation Frequency

100

975 MHz

Microphone Frequency

2

Temperature

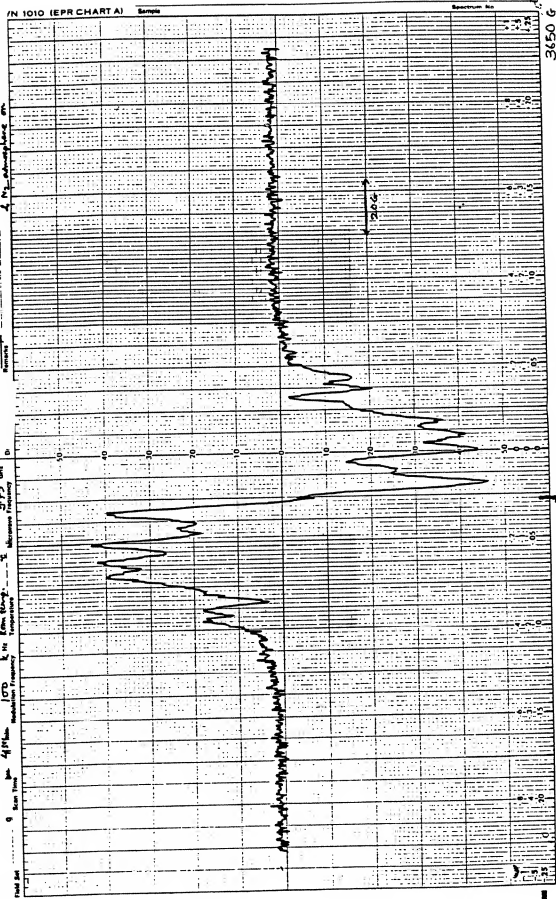
100

Modulation Frequency

100

Modulation Frequency

100



3480.43G
= 19.5G

Time Constant 1.20 msec; Modulation Amplitude 2.5 $\times 10^{-4}$ g; Microwave Power 1 watt
 Scan Range 0; Scan Time 4.0 sec; Microwave Frequency 9.35 GHz; Microwave Frequency 9.35 GHz

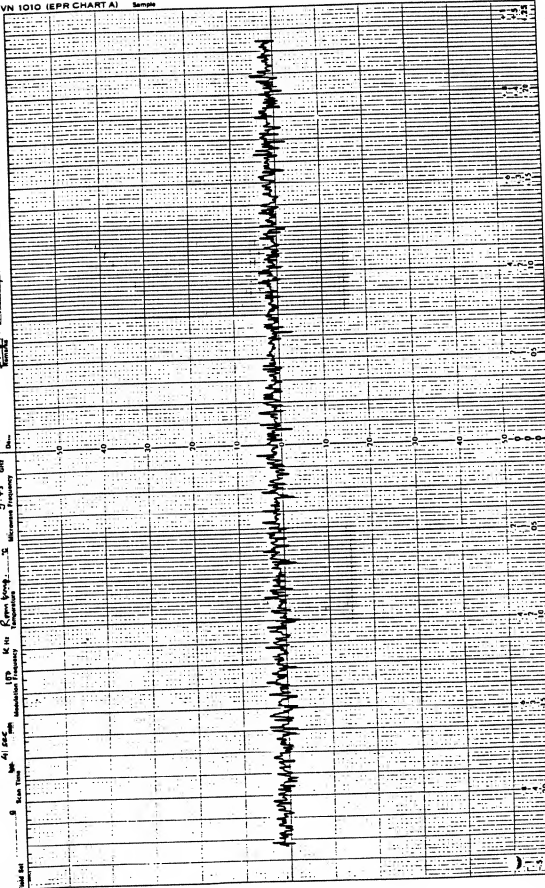
Time Modulation for Penetration

Sample: 60% Benzene/40% Hexane No. 100

VN 1010 (EPR CHART A)

Sample

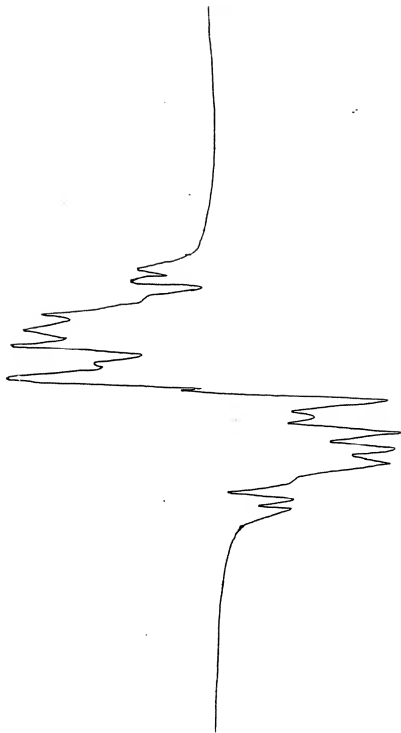
Spectrum No.



3650 G

3650 G

MIRROR IMAGE OF ESR SPECTRUM OF UHMWPE IRRADIATED AT RT/N₂ ATM.



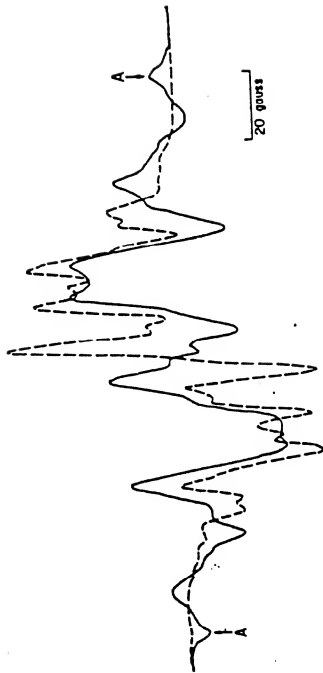


Figure 2. ESR spectra of allyl free radicals (dotted curve) and of mixed allyl and allyl free radicals after heating to room temperature (solid curve). Decay of allyl free radicals was calculated from height of peaks marked A.

REFERENCE: D.C. Waterman and M. Dole, *J. Phys. Chem.*, 74(9), 1970, 1913-1922